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Gold-Precious Metals Keynote

DEALING WITH COPPER IN GOLD ORES; IMPLEMENTED AND FUTURE APPROACHES

By

Dr Paul Breuer

Gold Processing Team Leader
CSIRO Mineral Resources Flagship, Australia

Presenter and Corresponding Author

Paul Breuer
paul.breuer@csiro.au

ABSTRACT

Cyanidation via heap leach or carbon-in-leach (CIL) / carbon-in-pulp (CIP) has become the predominant gold processing and recovery technique adopted since the late 1970's. A major advantage of cyanidation compared to the chlorine/chloride method used prior to the advent of cyanidation (and many alternative lixiviants) is the selectivity for gold (and silver) over most other metals. However, the selectivity over copper is often poor as most of the copper minerals commonly associated with gold, including sulfides (chalcopyrite being an exception), oxides, carbonates and native copper, are readily dissolved in the cyanidation process. The dissolution of copper impacts the cyanidation process economics, at the very least as additional cyanide is required to complex the copper (in addition to the gold). In addition downstream issues may arise and there may be increased cyanide destruction costs.

Due to the dwindling resources of simple cyanide extractable gold deposits, a large proportion of the gold processed in the 21st century will be recovered from lower grade and more complex gold ores, many of which will contain cyanide soluble copper minerals. By way of example, the data for Australia (from 2012) indicates a significant opportunity for gold recovery from iron oxide copper-gold (IOCG) deposits, which contain 24.7% of the inferred gold resources but only contribute 3.9% of gold production in Australia. In comparison, other (non IOCG) copper-gold deposits in Australia containing 12.4% of the inferred gold resources and have contributed 25.2% of gold production from these deposits.

The main approaches considered to treat copper-gold ores or gold ores containing copper are:

1. Flotation to generate a copper concentrate containing gold as a co-product and cyanidation of the flotation tail and/or other concentrate streams to recover additional gold.
2. Cyanidation of selectively mined ore having low soluble copper.
3. Preleach of copper before cyanidation.
4. Minimising/reducing copper dissolution during cyanidation.
5. Cyanidation with cyanide (and copper) recovery.
6. Alternatives to cyanidation for gold recovery.

This paper describes the various approaches and the large number of processing options that have been considered to treat gold ores with cyanide soluble copper. Notably, flotation has been mostly adopted, particularly for ores containing copper sulfide, with cyanide recovery rarely implemented. A number of approaches and processing options, that are yet to be demonstrated on a commercial scale, have potential for adoption in the future as the industry strives to process more challenging copper-gold and copper containing gold ores.

Ultimately, there is no universal process solution for dealing with copper in gold ores and the most profitable processing approach is highly dependent on the mineralogy and metal grades of the ore.

INTRODUCTION

The gold mining industry has undergone significant change in the past century through the development of new hydrometallurgical processes and technologies which have delivered safety and environmental improvements, and allowed the extraction of gold that couldn't be recovered by gravity methods used prior to this time. The most significant was the development of cyanidation for gold recovery via heap or carbon-in-leach (CIL) / carbon-in-pulp (CIP) and its predominant adoption since the late 1970's.

The major advantage of cyanidation compared to chlorine/chloride, which was used prior to the advent of cyanidation, is the selectivity for gold (and silver) over most other metals. The exception to this is copper as most of the copper minerals commonly associated with gold, including sulfides (chalcopyrite being an exception), oxides, carbonates and native copper, are readily dissolved in the cyanidation process. The dissolution of copper significantly impacts the cyanide demand as additional cyanide is required to complex the copper (in addition to the gold). Cyanide is also oxidised to cyanate by Cu(II) present in the ore and by oxygen (catalysed by the presence of copper and activated carbon). There can also be additional downstream costs such as increased reagents for cyanide destruction. These factors can make the cyanidation process uneconomic for gold recovery.

The use of toxic mercury to collect gold via amalgamation has also been replaced by cyanidation in developed countries, but is still used by some small miners in undeveloped countries where efforts continue to be made to eliminate the practise. Cyanide is also toxic, particularly to aquatic life, but is less hazardous to handle than chlorine and mercury. There have also been significant improvements in the last 20 years in the transportation, storage, handling and use of cyanide, and the development of an industry code of best practise (www.cyanidecode.org) to enhance the sustainability of cyanidation for gold recovery.

The effectiveness of cyanidation to recover gold is largely dependent on the ore mineralogy. Deposits are typically classified with respect to cyanidation as⁽¹⁾:

- Free-milling - readily amenable to cyanidation;
- Complex - economic but require significantly higher reagent additions; or
- Refractory – by exception those with poor gold recovery or uneconomic.

Commonly gold deposits are refractory due to:

- (i) Gold encapsulated in sulfide minerals;
- (ii) Presence of carbonaceous material (Preg-robbing); and/or
- (iii) Presence of high soluble copper.

As the availability of free-milling ores has declined the industry has looked to process the more complex and difficult to treat refractory ores. Methods have thus been investigated and developed to pre-treat refractory ores to make them amenable to cyanidation. Gold encapsulated in sulfide minerals is today pre-treated by either roasting, pressure oxidation, bio-oxidation, ultrafine grinding or ultrafine grinding with atmospheric oxidation⁽²⁾. Preg-robbing ores are pre-treated by roasting or at low carbonaceous content the preg-robbing material can be blinded by an organic reagent like kerosene. No universal solution exists to deal with high soluble copper containing gold ores, though many processing solutions have been proposed and investigated. Some approaches to deal with soluble copper have been implemented, but these are specific to the copper mineralogy or gold extraction process (heap leach or CIL/CIP).

This paper reviews the recovery of gold using cyanide from ores containing copper (including copper-gold ores) and the research and development of approaches to dealing with high soluble copper during cyanidation of these ores or derived process streams (eg. copper flotation tails).

COPPER MINERALISATION ASSOCIATED WITH GOLD

Due to the dwindling resources of simple cyanide extractable gold deposits, a large proportion of the gold processed in the 21st century will be recovered from lower grade and more complex gold ores, many of which will contain cyanide soluble copper minerals. By way of example, the 2012 data for Australia shown in Table 1 indicates almost 60% of economic demonstrated resources (EDR) for gold are associated with copper resources or have significant copper associated. There is clearly a significant opportunity for future gold recovery from iron oxide copper-gold (IOCG) deposits, which contain 29% of the EDR of gold, but only contribute 3.9% of gold production. In comparison, other (non IOCG) copper-gold deposits (essentially sulfide deposits) in Australia containing 29.4% of the EDR and contribute 25.2% of gold production.

A list of the major Cu-Au and IOCG resources being mined in Australia and the processing route are shown in Table 2. Notably flotation is used in all cases to generate a copper + gold concentrate with cyanidation only utilised at some sites to recover gold from the flotation tails or secondary streams.

Table 1: Australian economic demonstrated resources, inferred resources and mine production of gold for 2012 categorised by deposit type⁽³⁾.

Deposit Type	EDR gold		Inferred Resources		Mine Production	
	Tonnes	%	Tonnes	%	Tonnes	%
Lode Au Archean	2668	26.9	1579	34.6	136	54.3
Lode Au Proterozoic	788	8.0	411	9.0	13	5.3
Lode Au Phanerozoic	187	1.9	610	13.3	12	5.0
Iron Oxide Cu Au (IOCG)	2871	29.0	1127	24.7	10	3.9
Cu-Au (Other)	2918	29.4	567	12.4	63	25.2
Polymetallic base metals	258	2.6	145	3.2	5	2.0
Other	167	1.7	103	2.2	11	4.5

Table 2: Major Australian Cu-Au and IOCG resources currently being mined⁽⁴⁾.

Deposit	EDR ore (Mt)	Cu grade (%)	Au grade (g/t)	Processing route
Iron oxide Cu-Au (IOCG)				
Olympic Dam	6929	0.96	0.38	Cu (+Au) flotation with smelting and refining, U + Cu leach of tails
Ernest Henry	156	1.15	0.60	Cu (+Au) flotation
Prominent Hill - Cu/Au	126	1.29	0.53	Cu (+Au) flotation
- Au only	37	0.10	1.00	
Cu-Au				
Cadia East	4100	0.28	0.45	Gravity gold & Cu (+Au) flotation
Cadia Hill	420	0.17	0.43	
Ridgeway	220	0.31	0.69	
Boddington	715	0.11	0.66	Gravity gold, Cu (+Au) flotation & CIL of tails
Telfer - Open cut	332	0.09	0.69	Gravity gold, Cu (+Au) flotation & Au (pyrite) flotation/CIL
- Underground	158	0.29	1.34	
- West Dome	243	0.06	0.67	
Northparkes	471	0.58	0.21	Cu (+Au) flotation

Many gold deposits in the other categories also contain copper, but the copper grade is low such that these are not considered a copper resource associated with the gold resource. The extent of cyanide soluble copper in some of these gold deposits is significant and can be one to two orders of magnitude greater than the gold content. In the majority of cases the gold can still be recovered economically by cyanidation despite the cyanide soluble copper increasing cyanide consumption and reagent needed to destroy the copper cyanide before discharge of the cyanidation tails into the tailings storage facility.

The main copper minerals associated with gold are shown in Table 3. The Table also shows their reactivity in a typical cyanide leach solution and the amount of cyanide lost by reaction with the copper mineral. Notably, all the copper minerals are leached by cyanide to varying degrees, ranging from 5% to 10% for chalcopyrite to >90% for most of the oxide copper minerals along with covellite and chalcocite⁽⁵⁾. These minerals consume 30-50 kg NaCN / t ore for every 1% reactive copper present, which often makes conventional cyanidation of copper–gold ores uneconomic.

Table 3: Solubility of copper minerals in 0.1% NaCN solutions.

Mineral	Formula	% Cu dissolved in 24 hr ^a		Cu dissolved at room temp. in 6 hr ^b	
		23 °C	45 °C	% Cu	g NaCN/ g Cu
Chalcopyrite	CuFeS ₂	5.6	8.2	5.8	2.79
Chrysocolla	CuSiO ₃ ·nH ₂ O	11.8	15.7	—	—
Tetrahedrite	(Cu,Fe,Ag,Zn) ₁₂ Sb ₄ S ₁₃	21.9	43.7	—	—
Enargite	Cu ₃ AsS ₄	65.8	75.1	—	—
Bornite	FeS·2Cu ₂ S·CuS	70.0	100.0	96.0	5.13
Cuprite	Cu ₂ O	85.5	100.0	96.6	4.94
Native copper	Cu	90.0	100.0	—	—
Covellite	CuS	—	—	95.6	5.15
Chalcocite	Cu ₂ S	90.2	100.0	92.6	2.76
Malachite	2CuCO ₃ (OH) ₂	90.2	100.0	99.7	4.48
Azurite	2Cu(CO) ₃ ·Cu(OH) ₂	94.5	100.0	91.8	3.62

^aData after Hedley and Tabachnick⁽⁵⁾.

^bData after Lower and Booth⁽⁶⁾. Cyanide consumption is per g of contained copper.

MINIMISING SOLUBLE COPPER IN FEED TO CYANIDATION

Given the impact soluble copper has on cyanidation, it is desirable to minimise or reduce the soluble copper in the feed to cyanidation. A number of flowsheet options for treating copper-gold and gold containing copper ores have been investigated, developed and implemented. A graphical presentation of the common processing options which can reduce the soluble copper in the feed to cyanidation are presented in Figure 1 (where the gold ore, gold concentrate and/or flotation tail are potential cyanidation feed streams). These processing options are discussed in more detail below.

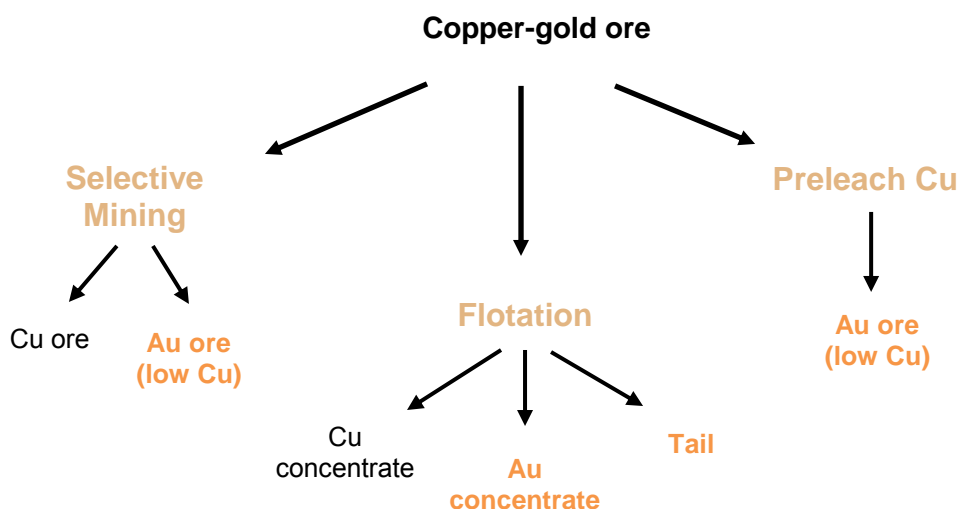


Figure 1: Flowsheet options in the processing of copper-gold and gold containing copper ores to reduce the soluble copper in cyanidation.

Selective Mining

Depending on the distribution of gold and copper in the ore body there may be the ability to selectively mine the deposit to produce one or more of the following feed streams:

1. Gold ore with low soluble copper (and thus amendable to direct cyanidation);
2. Copper ore; and/or
3. Gold ore with high soluble copper.

If selective mining can produce streams 1 and/or 2 then processing may be relatively straight forward by conventional means. Depending on the quantity of material in these selectively mined streams, processing may be conducted in separate or integrated circuits, or in campaigns through the same plant with optimised conditions for each feed. Selective mining may however limit the recovery from the resource if material is rejected and not processed.

Selective mining has been used at the Red Dome Gold Mine in Australia to selectively mine and cyanide leach material containing less than 0.5% copper, with the high copper material being stockpiled for future processing⁽⁷⁾.

Selective mining and campaign processing is used at Telfer where the flotation circuit is operated to produce a bulk Cu-Au concentrate, a sequential Cu-Au and Au-pyrite concentrate or pyrite only concentrate depending on the feed to the concentrator⁽⁸⁾.

Flotation

Flotation was introduced for the treatment of base metal sulfide ore in the early 19th century which quickly led to flotation being used to recover and concentrate gold bearing sulfides and free gold. Today, flotation is commonly used in the processing of primary copper-gold ores to produce a copper concentrate containing gold as a co-product (Table 2), where the gold is recovered as a by-product of copper smelting and refining⁽⁹⁾. The gold is usually discrete and either free, associated with copper sulfides or associated with iron sulfide minerals. Due to this variable gold association, significant gold is often not recovered with the copper concentrate and treatment of the tails or generation of other concentrate streams (such as a pyrite concentrate) is needed. Depending on the gold and soluble copper concentration in the flotation tails or gold concentrate streams, these may be treated economically by cyanidation to recover additional gold. Optimisation of flotation in this case is to minimise cyanide soluble copper in streams proceeding to cyanidation (as opposed to maximising gold recovery with copper in the concentrate when the copper concentrate is the only stream from flotation which gold is recovered).

Flotation and smelting is preferred for copper sulfide ores, but as yet there is no practical alternative to cyanidation for copper oxide ores. IOCG deposits however are often amenable to flotation to generate a Cu-Au concentrate, with the recovery improving down through the orebody from the oxide zone to the transition and primary zones.

For oxidised and transition copper-gold ores it is difficult to obtain an acceptable copper concentrate. The two most common approaches are controlled potential sulfidisation (CPS) and the fatty acid flotation method⁽¹⁰⁾. The selected method is dictated by the nature of the mineral makeup of the gangue which is often complex and can play a significant role in the overall flotation efficiency. It has not been possible to prescribe a set method for the flotation of various ore types with each ore having to be evaluated on an individual basis in order to arrive at an acceptable flotation technique.

Preleach of Copper

The selective leaching of copper prior to cyanidation for gold can be achieved using reagents such as dilute acid, iron(III), copper(II)/chloride or ammonia⁽¹¹⁾. The simplest method of copper extraction using sulfuric acid however is applicable only to ores containing oxidised copper minerals, such as malachite, azurite and chrysocolla. Generally these processes are uneconomic in treating low grade copper ores, particularly sulfide ores, due to the high reagent consumption, neutralisation required before cyanidation (other than with ammonia) and/or issues with recovery of the leached copper.

Preleaching with limited cyanide addition such that the reactive copper minerals dissolve with little or no free cyanide remaining in the leach solution was proposed by Scerici⁽¹²⁾⁽¹³⁾. This establishes a chemical environment which minimises the leaching of the precious metals and enhances the adsorption kinetics for copper cyanides on activated carbon. Further cyanide is subsequently added to the copper depleted leach slurry in a CIP or CIL circuit where gold leaching and adsorption can proceed under typical cyanidation conditions. The copper loaded carbon is eluted using moderate strength cyanide solution at ambient temperature. Cold stripping enhances the selectivity of copper elution over the elution of gold and silver. The gold and silver loading accumulates and thus the eluted carbon is periodically diverted to the gold elution circuit to recover the precious metals. The carbon eluate is then acidified to precipitate the copper as CuCN which is subsequently digested to produce copper sulfate as a saleable product. The digestion of CuCN is discussed in detail below. This process, however, may not be as effective in treating ores containing slow leaching copper minerals such as chalcopyrite. A full scale demonstration plant was operated at the Mt. Gibson Gold mine in Australia for a period of time before being shut down due to "an interruption to the continuity of copper bearing ore supply"⁽¹²⁾. The absence of oxygen (or restriction of oxygen ingress) during the copper preleach with cyanide will also minimise gold dissolution. Recent work has shown that conducting the preleach under anoxic conditions results in greater dissolution of covellite and chalcocite⁽¹⁴⁾. Notable also in this work by Kyle *et al.*⁽¹⁴⁾ is the presence of sulfide ions in solution. Sulfide ions should be oxidised ahead of further cyanide addition to avoid cyanide loss as thiocyanate. Alternatively, if the preleach solution is separated from the ore and SART (discussed below) is used to separate/recover the copper and recycle the cyanide, the sulfide would reduce the require sulfide addition in the SART process.

Recent laboratory investigations have shown that glycine (with hydrogen peroxide) can selectively leach the copper minerals prior to cyanidation⁽¹⁵⁾. No information on reagent usage is provided.

CYANIDATION OF GOLD ORES WITH HIGH SOLUBLE COPPER

Much research and development has gone into approaches to economically treat via cyanidation gold ores with high soluble copper. These approaches are largely based around the recovery and recycle of cyanide (Figure 2). More detailed reviews of these processes have been published by Dai *et al.*⁽¹⁶⁾ and Sceresini⁽¹⁷⁾.

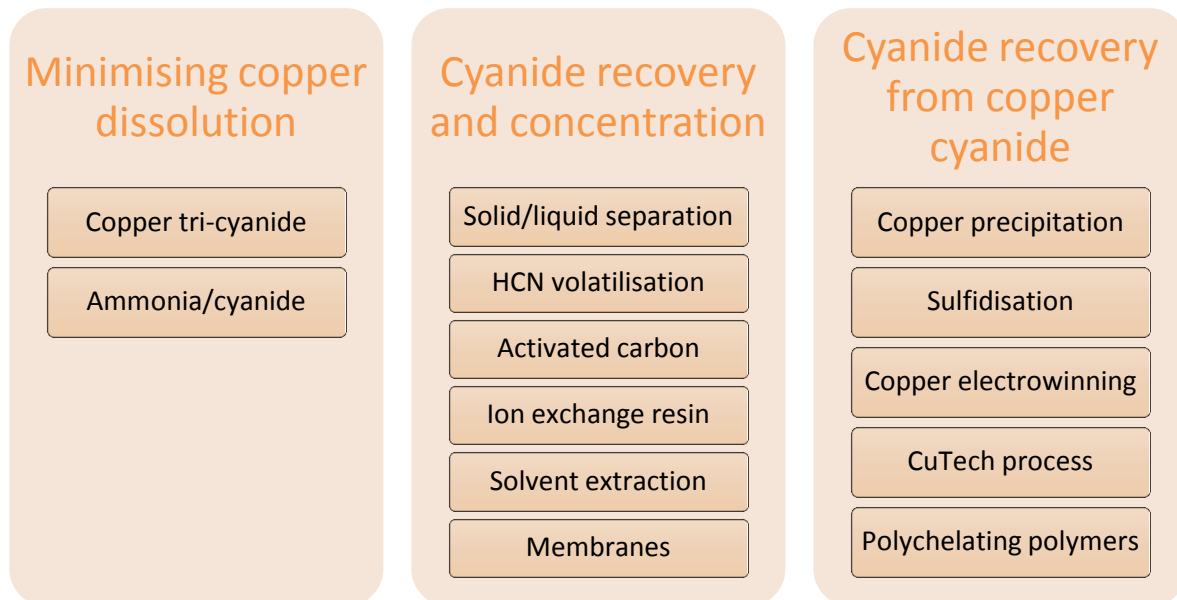


Figure 2: Approaches to economically treat by cyanidation gold ores with high soluble copper.

Many of these processes utilise the change in copper cyanide speciation and stability with pH and competing copper complexing agents (eg. ammonia and sulfide) to recover the cyanide. An example copper cyanide speciation as a function of pH is shown in Figure 3 where the cyanide which is not complexed with copper is present as cyanide ions above pH 10 and hydrogen cyanide (HCN) below pH 8.

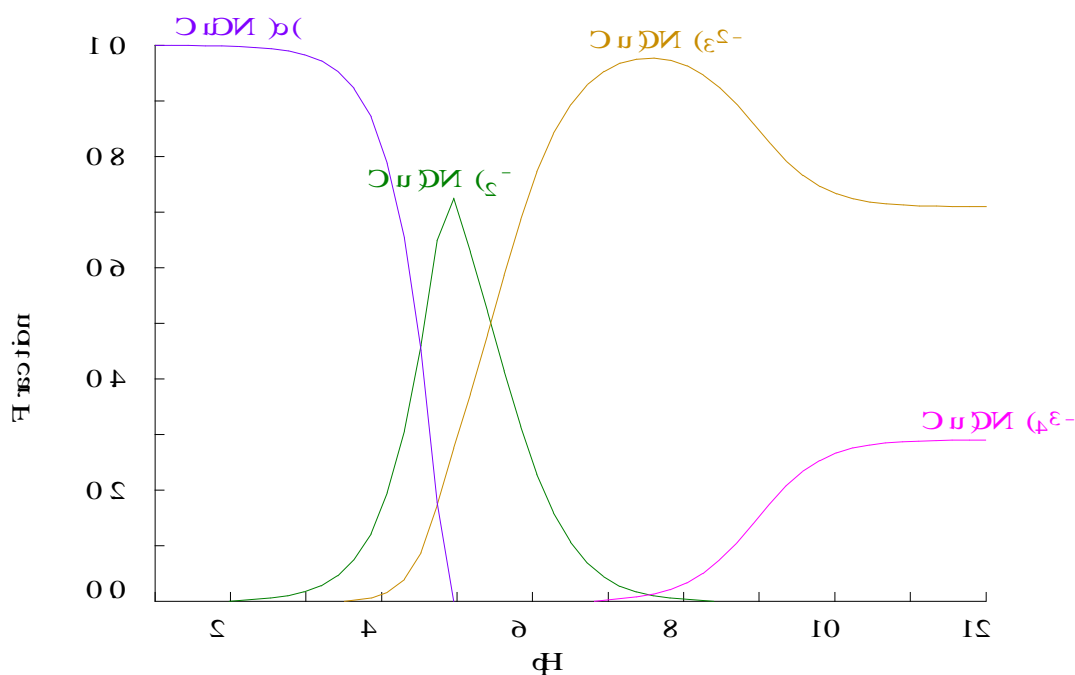


Figure 3: Copper cyanide speciation as a function of pH; 20 mM Cu with a CN:Cu molar ratio of 4.

Minimising Copper Dissolution

Minimising copper dissolution during cyanidation can be achieved by choosing reagent mixtures and conditions that render the copper minerals insoluble or slow to leach in comparison to gold. For example, the dissolution of common copper minerals in a leach solution containing copper tri-cyanide (no free cyanide ions) is much slower and incomplete as compared to complete

dissolution in a leach solution containing free cyanide⁽¹⁸⁾. The gold leaching process with copper tri-cyanide (Equation 1), however, is also much slower (Figure 4).

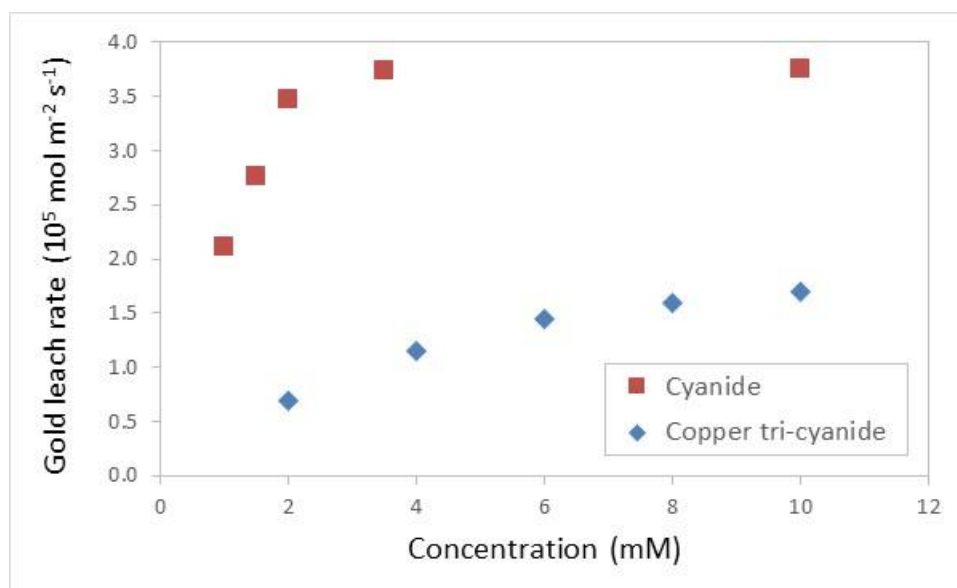
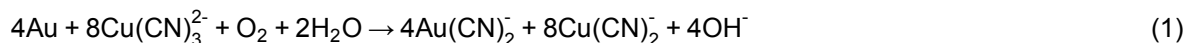


Figure 4: Gold (2 wt% Ag) leach rate measured in air saturated solutions using a REQCM.

There have been a number of studies into the application of the ammonia-cyanide process for the treatment of copper-containing ores, with a recent review published by Muir⁽¹⁹⁾. It has been shown that the addition of ammonia to the cyanide solution (with lower cyanide addition) results in a lower cyanide consumption and an increased selectivity of gold leaching over copper. The rate of gold leaching in this system is, however, apparently slower than that with free cyanide. Essentially the gold leaching in this system is conducted in the absence of free cyanide with copper tri-cyanide providing the cyanide for gold dissolution, as described above. However, with the presence of ammonia and copper, the gold oxidation reaction with copper tri-cyanide (Equation 1) is significantly enhanced⁽²⁰⁾. Considerations with the use of ammonia include losses due to volatilisation and its occupational health and environmental concerns; within Australia, ammonia is also reportable under the National Pollution Inventory.

Cyanide Recovery and Concentration

Cyanidation of gold ores with soluble copper is typically conducted with sufficient free cyanide concentration to minimise copper adsorption onto the activated carbon along with the gold (other than for the processes described in the previous section). Thus, it follows that consideration should be given to the recovery of cyanide as free and/or copper cyanide species. The recovery of copper along with cyanide is currently only possible from clear solutions and these processes are discussed in the next section – Cyanide recovery from copper cyanide. This section reviews the approaches for the recovery and concentration of cyanide from slurries (eg. CIL/CIP tails) or solutions (eg. heap leach solution or tailings storage facility decant).

The approaches discussed in this section are shown in Table 4. An important aspect of the processes, which use activated carbon or ion exchange (resin and solvent extraction), is that free cyanide ions are not recovered to any appreciable extent due to their poor adsorption/selectivity. Hence, these approaches often incorporate the addition and/or recycle of metal, metal salts or metal ions to complex the free cyanide ions and facilitate the recovery of free cyanide as metal cyanide.

Table 4: Approaches to recover and concentrate cyanide and copper cyanide species, and their applicability to slurries or solutions.

Approach	Species recovered	Slurry	Solution
Solid/liquid separation	Free cyanide and copper cyanides	Yes	Not applicable
HCN volatilisation	Free cyanide and copper cyanides	Yes	Yes
Activated carbon	Copper cyanides	Yes	Yes
Ion exchange resin	Copper cyanides and possibly free cyanide	Yes	Yes
Solvent extraction	Copper cyanides and possibly free cyanide	No	Yes
Membranes	Free cyanide and/or copper cyanides	No	Yes

Solid/Liquid Separation

Solid/liquid separation of slurries requires either a counter current decantation (CCD) circuit or filter to recover solution containing most of the cyanide and copper cyanide species. Often these capital expensive items (and downstream units needed to recover cyanide and copper) are not economically justified by the savings in reagent costs (both in cyanide and reagents to destroy cyanide if it is not recovered). A large number of thickeners and filters are used in the gold industry due to water balance issues, some of which are associated with cyanide recycle or recovery⁽²¹⁾.

HCN Volatilisation

Volatilisation processes take advantage of the volatility of hydrogen cyanide (HCN) and achieve separation by contacting acidified slurry or solution with air (by gas bubbling or use of a column contactor) to remove HCN gas. The HCN gas is then adsorbed from the air stream into an alkaline solution. This means cyanide is both separated and concentrated, potentially up to the solubility limit of sodium or calcium cyanide (depending on the use of caustic or lime). Several industrial processes exist based on this concept including the AVR process; the Cyanide Recovery Process (CRP); and the Cyanisorb process. A review of the AVR fundamentals and processes was recently published by Dai *et al.*⁽¹⁶⁾. A variant on the AVR process is proposed by Adams and Lloyd⁽²²⁾ to recover cyanide by tails washing and pond stripping (WPS process); with HCN stripped from the acidified solution in a covered process water pond by bubbling air.

While AVR technology can be used for slurries to recover cyanide, copper is precipitated as copper cyanide which is not recoverable and is discharged to the tailings which can have environmental implications. The processing of slurries is also more difficult with the volatilisation from a pulp requiring a significantly longer residence time to remove the hydrogen cyanide from solution. Additionally, all AVR studies with slurries reported increased acid consumption due to acid consuming constituents in the solids.

Activated Carbon

In treating copper-gold ores, a sufficient free cyanide concentration is typically maintained to encourage the selective adsorption of gold over copper onto carbon (other than for the processes described in the previous section which aim to minimise the dissolution of copper). To recover copper cyanide and free cyanide using carbon the solution speciation therefore needs to be modified to exploit the strong copper cyanide adsorption at low cyanide to copper ratios (ratio less than 3 where there is no free cyanide present). This can be achieved through the addition/dissolution of copper⁽²³⁾ or copper salts; the addition of Cu(II) salts however will result in the oxidation of one mole of cyanide to cyanate per two moles of copper added (eg. Equation 2).



Ion Exchange Resin

Strong base ion exchange resins adsorb metal cyanide complexes with little selectivity. Typically, the strongly adsorbed precious metals, such as gold and silver, can be separated from the base metals during elution. Gold selective ion exchange resins are available today which have improved selectivity of gold cyanide over base metal cyanides.

As the environmental guidelines imposed on the gold industry have become increasingly stringent in recent times, the use of ion exchange resins for cyanide management has received considerable attention. This has resulted in the development of several technologies utilising resins to recover metal cyanides, and particularly copper cyanides in the processing of copper-gold ores. The more notable technologies and their process characteristics are summarised in Table 5.

Table 5: Ion exchange resin based processes for cyanide recovery and concentration.

Process	Free CN ⁻ recovery	Eluant	Regen. Soln.	Issues	Application Level
Augment	yes (by CuCN ppt in pores during elution)	copper cyanide	H ₂ SO ₄	osmotic shock; resin blockage	pilot plant
Hannah	yes (Cu remaining in the resin and/or Zn/Cu added/ recycled to complex free CN)	cyanide	H ₂ SO ₄	osmotic shock; resin blockage	pilot plant
Vitrokele	limited	Zn(CN) ₄ ²⁻ or NaCN + NaOH	H ₂ SO ₄	poor Cu elution; resin blockage; AVR needed; osmotic shock	commercial plant
Elutech	limited	H ₂ O ₂ + H ₂ SO ₄	n/a	oxidation of cyanide; loss of resin capacity; osmotic shock	pilot plant

All the ion exchange resin based processes in Table 5 involve the use of acid for either resin elution or resin regeneration and thus have the issue of resin degradation and breakage due to osmotic shock and resin pore blockage due to the formation of copper cyanide and/or copper iron cyanide precipitates. Dai *et al.*⁽²⁴⁾ investigated a wide range of organic and inorganic eluents and developed a satisfactory chloride based elution method for strong base resins with a pH close to the loading conditions (pH 10-11) which avoids the problems created by the acidic eluents. This method involved a pre-soak of the loaded resin with 1 M NaCN followed by the elution with 4 M NaCl. Close to 90% of the copper was successfully eluted in only 2 bed volumes, resulting in a small volume of highly concentrated copper eluate which is suitable for downstream processing. The eluted resin in the chloride form is able to be recycled without regeneration. One drawback of this process, however, is that the cyanide used for pre-soak will have to be recovered, imposing an extra burden on the cyanide recovery process. The fate of iron cyanide in this chloride based elution process has not been addressed, but it is expected to follow the copper cyanides. Thiocyanate, which is generated in cyanidation from the reaction of cyanide with sulfide minerals, can be minimally or partially recovered using different elution flowsheets.

Solvent Extraction

Solvent extraction offers an alternative to ion exchange resins and activated carbon for concentrating cyanide and copper cyanide. Cyanide recovery by solvent extraction is improved by first complexing cyanide with a metal (as for activated carbon and ion exchange resins). Several processes based on solvent extraction have been proposed to recover copper from cyanide leach solutions.

Table 6: Solvent extraction processes for cyanide recovery and concentration.

Solvent extraction system	Load/strip conditions	Reference
LIX®7820 (mixture of Aliquat® 336 and 4-nonylphenol)	Extract: pH 10 or below. Strip: Alkali solution > pH 11.	Davis <i>et al.</i> ⁽²⁵⁾
LIX®7950 (tri-alkylguanidine extractant)	Extract: pH 11 or below. Strip: high pH-copper cyanide rich spent electrolyte.	Dreisinger <i>et al.</i> ⁽²⁶⁾ Xie and Dreisinger ⁽²⁷⁾

For both LIX®7820 and LIX®7950, the extraction efficiency decreases significantly with increasing copper content and with increasing CN:Cu ratio due to the preferential extraction of copper tri-cyanide over copper tetra-cyanide and cyanide⁽²⁸⁾. Recovering copper from solutions with too low a CN:Cu ratio (e.g. 2.2) results in the precipitation of CuCN in the organic phase⁽²⁹⁾. These extractants also strongly extract zinc and nickel cyanides, but the extraction of iron cyanide is poor. The presence of thiocyanate in the solution significantly depresses the extraction of copper; 50 mM thiocyanate was shown to decrease the copper cyanide extraction efficiency from ~100% to ~10%⁽³⁰⁾.

The use of solvent extraction for the recovery and concentration of copper cyanide from solutions thus faces several challenges. Degradation of expensive organics is always a concern for solvent extraction technologies but has received little attention in the application for copper cyanide recovery. The potential contamination of the raffinate by organics may cause problems, e.g. potential activated carbon fouling which reduces the efficiency of gold recovery if raffinate is recycled back to the leach circuit. The most significant problem, however, is the low extraction efficiency for the recovery of copper cyanide from solutions containing high copper and/or thiocyanate, and the continuous decrease in the extraction efficiency due to the increase in CN:Cu ratio through each extraction stage (copper content decrease with essentially unchanged free cyanide).

Membranes

A membrane is an interphase between two adjacent phases acting as a selective barrier, regulating the transport of substances between the two compartments. Passive transport through membranes occurs as a consequence of a driving force, i.e. a difference in chemical potential by a gradient across the membrane. Such processes include concentration (pervaporation and dialysis), pressure (gas separation, reverse osmosis, nanofiltration, ultrafiltration and microfiltration) or by an electrical field (electrodialysis). Membrane technologies have gained wide applications in the medical technology and water treatment industries, and have started to attract interest in the mining industry. Nevertheless, their application is limited at present due to the need for very clean solutions (free of solids and precipitates). As most of the solutions in mining are saturated in salts the impact of scaling is essentially unavoidable and a common issue. Some developments and applications of these technologies to concentrate or recover cyanide and copper cyanide are discussed below.

Engineered Membrane Separation (EMSTM) system developed by HW Process Technologies, Inc. enables the recovery of both cyanide and copper from copper cyanide containing solutions⁽³¹⁾. Its membrane component separates multi-valent salts (copper and base metal cyanide complexes) from mono-valent salts (cyanide, gold and silver cyanide complexes) via a nanofiltration mechanism. The permeate-to-concentrate ratio of this EMSTM treatment is typically 90:10. The nominal 10% by-volume bleed of 10 fold concentrated copper can be treated for copper recovery via electrowinning or SART. Whilst the 90% by-volume permeate containing precious metal cyanide complexes and cyanide ions can be subject to precious metal recovery via zinc cementation or a conventional carbon process, followed by recycling of the residual cyanide. This process has been tested in a pilot plant using the pregnant leach solution generated from a thin-layer on-off pad heap leach of agglomerated tailings at a mine site in Durango State, Mexico. The pilot plant test achieved 85 - 90% recovery of copper cyanide complexes in the concentrate and greater than 90% gold recovery in the permeate. The clarified feed solution in the pilot plant was processed through a standard sodium-cycle softener resin process to lower the calcium concentration to ~150 mg L⁻¹ prior to the EMSTM process to reduce the potential for precipitation of calcium salts (mainly CaSO₄ and CaCO₃) and fouling of the membrane.

Gas Membranes can be used to recover cyanide from cyanide containing solutions. The hydrophobic microporous membrane, e.g. polypropylene (PP) or polytetrafluoroethylene (PTFE), is used to separate two aqueous streams: the acidified cyanide containing stream and the cyanide stripping stream (e.g. NaOH). The membrane pores remain gas-filled (air) as long as the pressure difference between these two aqueous phases is less than the breakthrough pressure. The volatile HCN(aq.) is volatilised into and diffuses across the membrane gas layer into the strip solution where it reacts with NaOH to form NaCN. This gas membrane process has been used to recover cyanide from industrial wastewater streams⁽³²⁾. Most notable is that the volumetric mass transfer coefficient of a membrane contactor can be two orders of magnitude higher than that of an AVR reactor (gas bubbling), which enables a significantly faster cyanide recovery rate and/or reduced capital (and operating) cost compared to AVR⁽³³⁾. This technology is most suited to concentration of cyanide streams low in metal cyanides as metal cyanides can precipitate and block the membrane as the cyanide ions are depleted. An osmotic distillation effect (transfer of water) also occurs when the ionic strength is greatly different on each side of the membrane.

Cyanide Recovery from Copper Cyanide

A number of processes have been developed or proposed to recover cyanide from copper cyanide (Table 7). Other than the polychelating polymers and direct electrowinning, these technologies are based on acidification of the copper cyanide solution and/or acid digestion of CuCN. Thus, for every mole of cyanide recovered at least one mole of acid and one mole of alkali are required.

Table 7: Approaches to recover cyanide from copper cyanide.

Approach	Conditions	Cu form recovered
Cu precipitation	pH < 4	CuCN
SART	pH < 5 + S ²⁻	Cu ₂ S
Electrowinning	Directly or pH < 5	Cu metal
CuTech process	+ CuCl	CuCN
Polychelating polymers	Alkaline pH	Cu metal or soluble Cu ²⁺

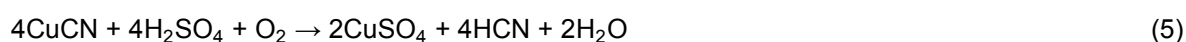
Copper Precipitation

Sufficient acid addition ultimately results in the formation and precipitation of copper cyanide (CuCN). Thus, in this situation some cyanide remains complexed with the precipitated copper which is either not recovered or requires an additional treatment step, such as acid digestion. Other precipitates can also form depending on the solution composition as shown in Equations 3 and 4.



The extent of precipitation and composition of the final precipitate depends on pH, HCN removal, iron concentration, and thiocyanate concentration in the solution⁽³⁴⁾. The formation of CuSCN and Cu₂Fe(CN)₆ is preferable over the formation of CuCN. This is because cyanide in the form of SCN⁻ and complexed with Fe is considered unrecoverable. Hence for every mole of Cu precipitated with these species formed one extra mole of cyanide is recovered compared to when CuCN is formed.

As the copper precipitate contains cyanide (mainly as CuCN), there is a loss of cyanide and problems marketing the precipitate as saleable copper. Sceresini and Richardson⁽¹²⁾ propose a digestion method that released hydrogen cyanide and oxidising copper to give copper(II) sulfate according to Equation 5. The CuCN precipitate is filtered and thoroughly washed to achieve a very low chloride level prior to the digestion with sulfuric acid and oxygen at about 75°C for 8 hours to produce copper sulfate solution for direct sale or for producing copper cathode via electrowinning. The HCN gas liberated during digestion is scrubbed by lime and recycled. This technique has been used at Mt Gibson for treating CuCN generated from the Sceresini process (described earlier).



The CuTech process, which is discussed in more detail below, uses a hydrochloric acid digestion to produce a cuprous chloride solution for recycle in the process or copper product by electrowinning or precipitation.

Sulfidisation

Like AVR, the sulfidisation processes involves acidifying the solution, but use sulfide to precipitate Cu_2S instead of producing CuCN . Such processes use sulfide ions from reagents such as Na_2S , NaHS , or H_2S , or biogenically produced H_2S to produce a copper sulfide precipitate (Equation 6).



Two processes exist which exploit this chemistry and only differ in terms of the precipitate handling. They are the Metallgesellschaft Natural Resources (MNR) process⁽³⁵⁾ and the SART process⁽³⁴⁾. The MNR process uses only filtration for post precipitation dewatering, requiring large filtration machines as the slurry can be as low as 0.5% solids. The SART process instead thickens the slurry to 10–15% facilitating more than a 100 times decrease in slurry volume and hence filter size. The SART process also uses some of the thickened slurry as seed during precipitation, promoting crystal growth.

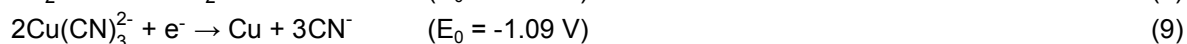
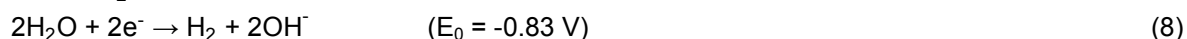
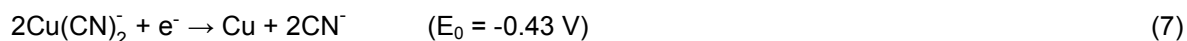
The sulfidisation reaction (Equation 6) is rapid and goes to near completion with stoichiometric sulfide addition at pH less than 5. The sulfidisation processes thus has several advantages over volatilisation processes such as reduced residence time and increased cyanide recovery. As cyanide is not separated from other aqueous species after sulfidisation is performed, SCN^- and some metal cyanides, such as iron cyanides, can build up in the circuit. Cyanide concentration processes, such as volatilisation or gas membrane, could be used subsequent to sulfidisation to address the build-up of these species and the positive water balance if a CCD circuit is used to generate the solution feed to the sulfidisation process. Excess sulfide addition results in SCN^- generation and thus cyanide loss.

SART processes have been flagged with poor copper recoveries / much greater than stoichiometric sulfide addition rates, which has not been seen in published laboratory or pilot plant testwork. This had remained a mystery until recently when it was found that the copper sulfide precipitate undergoes oxidation over time under the acidic conditions in the SART circuit⁽³⁶⁾. This oxidation either results in copper redissolution or necessitates addition of excess sulfide to avoid copper redissolution.

Copper Electrowinning

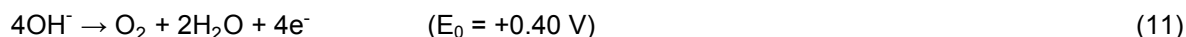
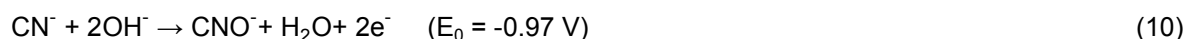
The electrochemical reactions occurring at the cathode during electrowinning of copper from a copper cyanide solution are shown in Equations 7-9 (where E_0 is the standard reaction potential at 25°C). The electrowinning of copper from alkaline cyanide solutions suffers from low current efficiencies and high energy consumption due to $\text{Cu}(\text{CN})_3^{2-}$ being the dominant copper species whose standard reduction potential is more negative than that of hydrogen evolution. Even if the initial solution mainly contains $\text{Cu}(\text{CN})_2^-$, the most electroactive copper cyanide species, the current efficiency drops sharply initially as the copper is deposited from solution due to the increase in the CN:Cu ratio from the released cyanide ions shifting the copper cyanide speciation to $\text{Cu}(\text{CN})_3^{2-}$, a less electroactive species.

Cathode reactions:



Another issue with using a conventional electrowinning cell to separate copper from cyanide is the oxidation of cyanide at the anode, which occurs preferential to oxygen evolution (Equations 10 and 11). This is advantageous as a waste water treatment process as the cyanide is also being destroyed, but undesirable for a cyanide recovery process. The use of sulfite can act as a sacrificial species to reduce the anodic destruction of cyanide, however this does not totally eliminate cyanide oxidation and the effectiveness decreased with increasing CN:Cu ratio⁽³⁷⁾.

Anode reactions:



A process using a DuPont cation exchange membrane in the electrowinning cell was developed and patented (often referred to as the DuPont process) to recover copper and cyanide from copper cyanide solutions. The use of the membrane avoids contact of cyanide and copper cyanide with the anode and thus loss of cyanide. However, the poor efficiency of the process due to hydrogen evolution remained. The use of sulfide, thiourea, thiocyanate, benzothiazole or thiosulphate was recommended to reduce hydrogen evolution at the cathode by blocking/poisoning the catalytic sites. Table 8 summarises the results from a number of published electrowinning investigations. Importantly, only high current efficiencies are achieved at high copper concentrations and low recoveries with the process being much less efficient at higher percentage copper recoveries. The use of elevated temperature improves the current efficiency, however the hydrolysis of cyanide ions is accelerated and becomes significant at temperatures above 50°C. The current efficiency can be improved with integration of electrowinning with a cyanide recovery process, such as AVR or a gas membrane. Such a process has been described by Dreisinger *et al.*⁽²⁹⁾ which takes a bleed stream from the electrowinning cell for cyanide recovery using the AVR process with the CuCN precipitate returned to the electrowinning process to lower the CN:Cu ratio and thus to encourage the formation of $\text{Cu}(\text{CN})_2^-$.

The problem of low current efficiency and high energy consumption with copper electrowinning from alkaline cyanide solutions can potentially be solved by conducting the electrowinning at low pH to increase the concentration of the most electroactive species, $\text{Cu}(\text{CN})_2^-$ (Figure 3), and thus minimise the hydrogen evolution side reaction⁽⁴²⁾. An advantage of electrowinning the copper at low pH is that the cyanide ion released during electrowinning will form HCN when there is sufficient H^+ available in the solution, thus avoiding a change in the copper cyanide speciation. The optimum pH for electrowinning was found to be pH 5 and acetate can be used as a pH buffer to minimise the interfacial pH change at the electrode surface with the release of cyanide ions from copper during copper deposition. This significantly enhances the electrowinning performance with a current efficiency of 90 – 100% and an average energy consumption of 0.85 – 1.00 kWh (kg Cu)⁻¹ achieved using this low pH electrowinning method and a membrane cell; which outperforms all the alkaline electrowinning methods employed by other researchers (Table 8). The released cyanide as HCN can be recovered by a hydrophobic gas membrane contactor or AVR process in conjunction with electrowinning to further improve performance. The use of a membrane cell is still necessary for acidic conditions despite the released cyanide being present as HCN, since the oxidation of copper cyanide at the anode is still significant and attempts to add a sacrificial species to replace or suppress this reaction have not proven successful.

Table 8: Copper electrowinning performances from alkaline copper cyanide solutions.

Researcher	Cu (mM)	CN:Cu	Temp. (°C)	Current density (A m ⁻²)	Cu recovery (% / h)	Current efficiency (%)	Power consumption (kWh kg ⁻¹)
Lu <i>et al.</i> ⁽³⁸⁾	15-30	3-9	40	-	40 / -	50-80	1-2
Fleming <i>et al.</i> ⁽³⁹⁾	80	2.9	ambient	-	25 / -	82	2.4
Wang <i>et al.</i> ⁽⁴⁰⁾	195	~4.4	50	7.5	68 / 8	76.5	3
Lemos <i>et al.</i> ⁽⁴¹⁾	10	3.5	ambient	0.185	99 / 5	1.5	79

CuTech process

The CuTech process was developed as a means for recovering gold and copper from pregnant cyanidation solutions with cyanide recycle⁽⁴³⁾. The process recovers cyanide and metal cyanides using cuprous chloride to precipitate insoluble metal cyanides (eg. AuCN and CuCN) from solution. The precipitate is then acid digested to recover cuprous chloride in the liquid phase and hydrogen cyanide in the gaseous phase. Any gold remains in the undigested solids which can be smelted. The cuprous chloride is recycled to precipitation with excess copper recovered by electrowinning or precipitation.

Polychelating Polymers

Non-toxic, long-chain water-soluble polymers containing significant concentrations of nitrogen, oxygen and/or sulphur groups are capable of complexing with anionic metal cyanide species⁽⁴⁴⁾⁽⁴⁵⁾. If the charge density of the polymer is sufficiently high, the metal may be displaced from the accompanying cyanide ions (copper atoms more strongly co-ordinate with the lone pair of electrons present at N, S and O sites within the polychelating polymer than to cyanide ions). The extent of cyanide displacement from the metal is dependent on the metal species, the polymer used and concentrations of cyanide, metal and polymer (the result of a series of equilibria between these species). Due to oxidation by oxygen in the solution both Cu(I) and Cu(II) valency states have been found to exist in the copper-polychelator speciation.

In the patented process by Smith and Robinson⁽⁴⁴⁾, membrane ultrafiltration was used to separate the metal-polychelator complex (retentate) from the cyanide ions (permeate). The cyanide is directly recycled to the leach circuit. The metal ions are released from the polymer, using dilute acid, metal ion oxidation state adjustment, or competing chelating agents. The copper can alternatively be recovered by conventional electrowinning directly from the polychelated copper polymer solution, releasing the polychelator for recycling⁽⁴⁵⁾. However, the contamination of foreign metal ions such as iron can significantly affect the current efficiency of copper electrowinning via the Fe^{2+}/Fe^{3+} redox couple.

To potentially enable the use of this technology to recover metal cyanides from leach slurries rather than clarified solutions, Jay incorporated the poly(alkyleneimine) polymers into a solid insoluble polymer (insoluble) and proposed a polymer-in-pulp process in which copper is recovered via polychelation and cyanide is potentially released simultaneously⁽⁴⁶⁾.

The polychelating processes are yet to be tested industrially.

ALTERNATIVES TO CYANIDATION FOR TREATING GOLD ORES WITH HIGH SOLUBLE COPPER

Lixiviant systems like chlorine/chloride, bromine/bromide, iodine/iodide, Fe(III)/thiourea, Fe(III)/thiocyanate, Cu(II)/thiosulfate and peroxide/glycine have all been examined for copper-gold ores but either readily react with copper minerals like cyanide, or the lixiviant is decomposed by Fe(III) or Cu(II) ions in solution (Table 9).

Compared to the chlorine/chloride system, bromine/bromide and iodine/iodide would appear to have some potential for oxidised copper-gold ores under neutral pH conditions, but testwork has indicated that the consumption and cost of reagent is high due to absorption onto the ore and precipitation of insoluble CuBr or CuI. Little has been reported on the use of these reagents on practical ores, although several fundamental and laboratory studies have been carried out.

Thiocyanate is oxidised by Fe(III) needed to leach gold and oxidised copper minerals react consuming acid and can precipitate CuSCN. Hence, does not appear a suitable system for copper-gold ores. Acidic thiourea is also not suited for oxidised copper minerals because of acid consumption and the reaction of Cu(II) with thiourea.

Thiosulphate and glycine are the only alkaline leaching systems for gold leaching besides cyanide. A copper-ammonia-thiosulfate system for leaching gold concentrates with high cyanide soluble copper has been proposed⁽⁵⁰⁾. Copper is also leached and recovered in this system, however, thiosulfate consumption can be high depending on the concentrate being treated. The peroxide/glycine system was indicated early to selectively leach copper from copper-gold ores⁽¹⁵⁾ but can also leach gold at elevated temperatures⁽⁵¹⁾. These systems have only been investigated in the laboratory and are yet to be piloted.

Table 9: Alternative lixiviant systems for treating copper-gold ores.

Lixiviant system	Reaction with Cu	Reference
Chlorine/chloride	Readily reacts with all sulfide minerals Requires pH<4 which dissolves copper oxides	Hiskey & Atluri ⁽⁴⁷⁾
Bromine/bromide (K-Process)	Readily reacts with all sulfide minerals Requires pH<6 but can form insoluble CuBr. Some selectivity over Cu oxides/metal.	Hiskey & Atluri ⁽⁴⁷⁾ Sehic ⁽⁴⁸⁾
Iodine/iodide	Reacts with most copper sulfides Leaches gold pH 4-10, Eh = 0.5 V Forms insoluble CuI at low iodide levels	Hiskey & Atluri ⁽⁴⁷⁾
Fe(III)/Thiocyanate	Acidic conditions dissolve Cu oxides Forms insoluble CuSCN Limited extraction of gold	Barbosa-Filho & Monhemius ⁽⁴⁹⁾
Fe(III)/Thiourea	Acidic conditions dissolve Cu oxides and reactive sulfides. Readily forms Cu(I) thiourea complex Cu(II) oxidises/decomposes thiourea	Deschenes <i>et.al.</i> ⁽⁵⁰⁾
Cu(II)/Thiosulfate	Ammoniacal conditions dissolve some Cu oxides. Cu(II) oxidises thiosulfate	Dai <i>et al.</i> ⁽⁵¹⁾
Peroxide/Glycine	Reacts with copper minerals at room temp. Leaches gold at 50 °C. Reagent consumption unknown.	Oraby and Eksteen ⁽⁵²⁾

CONCLUSIONS

No universal process solution for dealing with copper in gold ores has been found. A large number of processing options have been investigated with a number of these having been implemented:

- Flotation is often used to produce a flotation tail or gold concentrate stream with reduce cyanide soluble copper.
- Ammonia/cyanide leach system has been adopted at a limited number of operations to minimise copper dissolution during cyanidation.
- AVR and SART have been used in a small number of cases to recover and recycle cyanide.

Advancements and potential future approaches to dealing with cyanide soluble copper in gold ores are likely to include:

- Flotation as the primary approach to separating and reducing the cyanide soluble copper associated with gold ores.
- Adoption of the SART process (or MNR) to increase with improved engineering to overcome inefficiency with thickening, and particularly for heap and dump leach operations or where Merrill-Crowe is used for precious metal recovery).
- Implementation of ion exchange resin or activated carbon processes for recovery of cyanide from cyanidation tails slurry (CIL/CIP processes), though application is limited by the quantity of soluble copper these processes can handle.
- Gas membranes to replace AVR to concentrate cyanide.

- Chloride and thiosulfate systems are the most promising alternative lixiviant systems to cyanidation. The thiosulfate system offers better selectivity for leaching gold over copper than the chloride or cyanide systems.

Ultimately, the most economic processing approach is highly dependent on the mineralogy and metal grades of the ore.

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REFERENCES

1. La Brooy, S.R., Linge, H.G. and Walker, G.S., "Review of gold extraction from ores", Minerals Engineering, 7(10), 1213-1242, 1994.
2. Dunne, R., "Challenges and opportunities in the treatment of refractory gold ores", ALTA 2012 Gold conference, 1-15, 2012.
3. Geoscience Australia, "Australia's Identified Mineral Resources 2013", Geoscience Australia, Canberra, 2014.
4. Geoscience Australia, "Australian atlas of minerals resources, mines and processing centres", Geoscience Australia. [www.australianminesatlas.gov.au/] Accessed April 2015.
5. Hedley, N. and Tabachnick, H., "Mineral Dressing Notes No. 23, Chemistry of cyanidation", American Cyanamid Company, USA, New Jersey, 1968.
6. Lower, G.W. and Booth, R.B., "Recovery of copper by cyanidation", Minerals Engineering, 17 (11), 56-60, 1965.
7. Ryan, M., "Operation of the Red Dome Heap Leach", Economics and Practice of Heap Leaching, AusIMM, 87-93, 1988.
8. Benson, M.A., Headley, C.R., Hille, S.O. and Jacob, N.P., "Differential flotation commissioning at Telfer", Proceedings of Ninth Mill Operators' Conference, AusIMM, 17-24, 2007.
9. La Brooy, S.R., "Copper-gold ore treatment options and status", Randol Gold Forum, 173-177, 1992.
10. Phetla, P. and Muzenda, E. "A multistage sulphidisation flotation procedure for a low grade malachite copper ore", International Journal of Chemical, Nuclear, Materials and Metallurgical Engineering, 4(9), 26-32, 2010.
11. Muir, D., La Brooy, S. and Cao, C., "Recovery of gold from copper-bearing ores". World Gold 89 - Gold Forum on technology and practices, Reno, Nevada, USA, 363-374, 1989.
12. Sceresini, B. and Richardson, P., "Development and application of a process for the recovery of copper and complexed cyanide from cyanidation slurries", Randol Gold Forum Cairns'91 Proceedings, 265-269, 1991.
13. Sceresini, B. and Staunton, W., "Copper/cyanide in the treatment of high copper gold ores", AusIMM Extractive Metallurgy Conference, 123-125, 1991.
14. Kyle, J. Aye, K., Breuer, P. and Meakin, R., "The dissolution of covellite and chalcopyrite in cyanide solutions", World Gold 2011, Proceedings of the 50th Annual Conference of Metallurgists of CIM, Montreal, Canada, 533-544, 2011.
15. Oraby, E. and Eksteen, J., "The selective leaching of copper from a gold-copper concentrate in glycine solutions", Hydrometallurgy, 150, 14-19, 2014.
16. Dai, X., Simons, A. and Breuer, P., "A review of copper cyanide recovery technologies for the cyanidation of copper containing gold ores", Minerals Engineering, 25, 1-13, 2012.

17. Sceresini B., "Gold-copper ores", *Advances in Gold Ore Processing*, Elsevier, Amsterdam, 789 – 824, 2005.
18. Breuer, P., Dai, X. and Jeffrey, M., "Leaching of gold and copper minerals in cyanide deficient copper solutions", *Hydrometallurgy* 78, 156– 165, 2005.
19. Muir, D., "A review of the selective leaching of gold from oxidised copper–gold ores with ammonia–cyanide and new insights for plant control and operation", *Minerals Engineering*, 24, 576-582, 2011.
20. Jeffrey M., Linda, L., Breuer, P. and Chu, C., "A kinetic and electrochemical study of the ammonia cyanide process for leaching gold in solutions containing copper", *Minerals Engineering*, 15, 1173–1180, 2002.
21. Adams, M., "Impact of recycling cyanide and its reaction products on upstream unit operations", *Minerals Engineering*, 53, 241-255, 2013.
22. Adams, M. and Lloyd, V., "Cyanide recovery by tailings washing and pond stripping", *Minerals Engineering*, 21, 501-508, 2008.
23. Dai, X. and Breuer, P., "Cyanide and copper cyanide recovery by activated carbon", *Mineral Engineering*, 22, 469-476, 2009.
24. Dai, X., Breuer P. and Jeffrey, M., "Comparison of activated carbon and ion-exchange resins in recovering copper from cyanide leach solutions", *Hydrometallurgy*, 101 (1-2), 48-57, 2010.
25. Davis, M., Sole, K., Mackenzie J. and Virnig, M., "A proposed solvent extraction route for the treatment of copper cyanide solutions produced in leaching of gold ores", *ALTA 1998 Copper Hydrometallurgy Forum*, Queensland, Australia, 20-21 Oct, 1998.
26. Dreisinger, D., Ji, J. and Wassink, B., "The solvent extraction-electrowinning of copper and cyanide using XI7950 extractant and membrane cell electrolysis", *Randol Gold Forum-Perth'95*, 239-244, 1995.
27. Xie, F. and Dreisinger, D., "Studies on solvent extraction of copper and cyanide from waste cyanide solution", *Journal of Hazardous Materials*, 169 (1-3), 333-338, 2009.
28. Xie, F. and Dreisinger, D., "Recovery of copper cyanide from waste cyanide solution by LIX 7950", *Minerals Engineering*, 27, 190-195, 2009.
29. Dreisinger, D., Wassink, B., Lu, J., De Kock, F., Ji, J., West-Sells, P. and Dunne, R., "Solvent extraction recovery of copper cyanide from spent gold mill effluents", *Cyanide: Social, Industrial and Economic Aspects*, TMS Annual Meeting, New Orleans, LA, 347-360, 2001.
30. Xie, F. and Dreisinger, D., "Copper solvent extraction from waste cyanide solution with lix 7820", *Solvent Extraction and Ion Exchange*, 27 (4), 459-473, 2009.
31. Lombardi, J. and Bernard, R., "HW process technologies, INC's engineered membrane separation (ems) of copper and gold in cyanide solutions", *Cyanide: Social, Industrial and Economic Aspects*, TMS Annual Meeting; New Orleans, LA, 341-346, 2001.
32. Shen, Z., Han, B. and Wickramasinghe, S., "Cyanide removal from industrial praziquantel wastewater using integrated coagulation-gas-filled membrane adsorption", *Desalination*, 195, 40-50, 2006.
33. Dai, X. and Breuer, P., "Comparison of AVR and gas membrane technology in cyanide recovery", *ALTA 2013 Gold conference*, 253-268, 2013.
34. Fleming, C., "Cyanide recovery", *Advances in gold ore processing*, Elsevier, Amsterdam, 703-727, 2005.
35. Potter, G., Bergmann, A. and Haidlen, U., "Process of recovering copper and optionally recovering silver and gold be leaching of oxide and sulfide containing materials with water soluble cyanides", *US Patent 4587110*, 1986.

36. Simons, A. and Breuer, P., "The impact of residence time on copper recovery in Telfer Gold Mine's cyanide recycling process", World Gold Conference, 189-195, 2013.
37. Lu, J., Dreisinger, D. and Cooper, W., "Anodic behaviour of alkaline solutions containing copper cyanide and sulfite on the graphite anode", Journal of Applied Electrochemistry, 32, 1109-1118, 2002.
38. Lu, J., Dreisinger, D. and Cooper, W., "Copper electrowinning from dilute cyanide solution in a membrane cell using graphite felt", Hydrometallurgy, 64, 1-11, 2002.
39. Fleming, C., Grot, W. and Thorpe J., "Hydrometallurgical extraction and recovery of copper, gold, and silver via cyanidation and electrowinning", US Patent 5667557, 1997.
40. Wang, B., Lan, X., Song, Y. and Li, Y., "Copper electrowinning from gold plant cyanide-containing solution", Materials Science Forum, 610-613, 41-47, 2009.
41. Lemos, F., Sobral, L. and Dutra, A., "Copper electrowinning from gold plant waste streams", Minerals Engineering, 19, 388-398, 2006.
42. Dai, X., Breuer, P. and Jeffrey, M., "Electrowinning of copper from copper cyanide solutions at low pH", ECS Transaction, 28 (6), 281-294, 2010.
43. Clarke, S., "The Cotech process", Processing of Gold-Copper Ores (Practical Aspects), Colloquium. AMMTEC Pty Ltd, Perth, 1991.
44. Smith, B. and Robinson, T., "Process for the displacement of cyanide ions from metal-cyanide complexes", US patent, 5643456, 1997.
45. Jay, W., "Copper-gold cyanide recovery systems", Cyanide: Social, Industrial and Economic Aspects, TMS Annual Meeting, New Orleans, USA, 317-340, 2001.
46. Jay, W., "Metal ion recovery", US patent, 2005/0040108A1, 2005.
47. Hiskey, J. and Atluri, V., "Dissolution of gold and silver in different lixiviants", Mineral Processing & Extractive Metallurgy Review, 4, 95-134, 1988.
48. Sehic, O., "An update on the K-Process", Randol Gold Forum, Perth, 184-187, 1988.
49. Barbosa-Filho, O. and Monhemius, A., "Leaching of gold in thiocyanate solutions", Parts 1-3, Trans Inst Min Metall. (Section C Min.Proc.Extr.Metall), 105-124, 1994.
50. Deschenes, G., Bernard, D., Prud'Homme, P. and LaForest, D., "A preliminary techno-economic evaluation of the extraction of gold from a chalcopyrite concentrate using thiourea", Minerals Engineering, 7(4), 435-448, 1994.
51. Dai, X., Breuer, P., Hewitt, D. and Bergamin, A., "Thiosulfate process for treating gold concentrates", World Gold 2013, 61-70, 2013.
52. Oraby, E. and Eksteen, J., "The leaching of gold, silver and their alloys in alkaline glycine-peroxide solutions and their adsorption on carbon", Hydrometallurgy, 152, 199-203, 2015.